
CONCLUSION

SUMMARY AND CONCLUSIONS

Research is being carried out with cathode materials like LiMn_2O_4 , LiCoO_2 and LiNiO_2 for achieving higher output voltage and higher capacity retention in Li-ion batteries. The present investigation was carried out to improve the electrochemical behaviour of LiMn_2O_4 by substituting small amount of the substituents at the Mn site. The electrochemical behaviour of the cathode materials depends on the compound and method of preparation of the compound.

Compared with LiMn_2O_4 powders, the capacity loss of LiMn_2O_4 thin film was very small, and showed good cycling behaviour. Thin film cathode material has some advantages over the pellet-type powder material as lithium ion has the capacity of diffusing across the shorter distance. Quasi-equilibrium charge/discharge is attained in a shorter time compared to pellet-type electrode. The grains of thin film are much smaller than the powders. These small grains greatly increase the effective surface area of electrode, which make the intercalation and deintercalation of lithium ion into and out of LiMn_2O_4 much easier, resulting in good cycling behaviour. If the thickness of thin film is small, the diffusion route of lithium ion inside the thin-film electrode is very short.

In the present investigation, a simple, low cost, polymer spray pyrolysis method is used to prepare the nanocrystalline thin film cathode materials.

The present work is mainly focused on the following:

1. To know the effect of PEG on the formation of nanocrystalline LiMn_2O_4 thin film cathode material in spray pyrolysis method.
2. To improve the structural stability of LiMn_2O_4 during prolonged cycling, using small amount of substituents such as Y^{3+} , Gd^{3+} and Nd^{3+} in the Mn site of LiMn_2O_4 and their effect in LiMn_2O_4 .

Physico and electrochemical characterization of the synthesized materials are summarized below:

The preparation of nanocrystalline cubic spinel LiMn_2O_4 thin films was carried out by conventional spray pyrolysis method and the polymer spray pyrolysis method using polyethylene glycol as a gelling agent and complexing agent. PEG played a vital role to prepare nanosize homogeneous particles. PEG enhanced the homogeneous mixing of metal cations. As it had electronegative ether oxygens in its long chain, it attracted the electropositive metal ions (Li^+ and Mn^{2+}). Li^+ and Mn^{2+} metal ions trapped homogeneously in the polymer and controlled the particle size. The particles of LiMn_2O_4 were kept at the nanolevel and free from agglomeration during the heating process. In the polymer spray pyrolysis process, using polyethylene glycol (PEG) as the polymeric additive, thin film with nanocrystalline particles were obtained.

The average particle size of both conventional spray pyrolysis and polymer spray pyrolysis were around $\sim 85\text{nm}$ and $\sim 450\text{nm}$, respectively. The initial discharge capacities for LiMn_2O_4 thin films prepared by conventional spray pyrolysis and polymer spray pyrolysis were 137mAh/g and 138mAh/g , respectively. The initial discharge capacities for both the systems were nearly the same. But at 25th cycle, the

capacity loss observed for polymer spray pyrolysis system was only 12.4%, whereas that for conventional spray pyrolysis system was 15%.

The prepared $\text{LiY}_y\text{Mn}_{2-y}\text{O}_4$ ($y = 0.01, 0.03$ and 0.05) thin film cathode materials by polymer spray pyrolysis were single-phase with the space group of $\text{Fd}\bar{3}\text{m}$. The $\text{LiY}_{0.05}\text{Mn}_{1.95}\text{O}_4$ precursor completely crystallized at 600°C . The particle nature of the prepared thin films was uniformly distributed. The average particle size of $\text{LiY}_{0.05}\text{Mn}_{1.95}\text{O}_4$ was around 93 nm. The charge/discharge curves at the 1st and 25th cycle of $\text{Li//LiY}_y\text{Mn}_{2-y}\text{O}_4$ ($y=0.01, 0.03, 0.05$) showed that the $\text{Li//LiY}_{0.01}\text{Mn}_{1.99}\text{O}_4$ gave first cycle discharge capacity of 138mAh/g, which faded to 127mAh/g in the 25th cycle, registering the capacity retention of 92%. The corresponding values for $\text{Li//LiY}_{0.03}\text{Mn}_{1.97}\text{O}_4$ were 133mAh/g, 120mAh/g and 90.2% and for $\text{Li//LiY}_{0.05}\text{Mn}_{1.95}\text{O}_4$ 129mAh/g, 116mAh/g and 89.9% respectively. The initial discharge capacity fell down with substituent content due to decrease in Mn^{3+} concentration with an increase in y value of $\text{LiY}_y\text{Mn}_{2-y}\text{O}_4$. The capacity loss observed for $\text{Li//LiY}_y\text{Mn}_{2-y}\text{O}_4$ from $y=0.01, 0.03, 0.05$ were 8%, 9.8%, 10.1%, respectively. Among the various compositions, $\text{LiY}_{0.01}\text{Mn}_{1.99}\text{O}_4$ showed good electrochemical performance than the other compositions.

The prepared $\text{LiGd}_y\text{Mn}_{2-y}\text{O}_4$ ($y = 0.01, 0.03$ and 0.05) thin film cathode materials by polymer spray pyrolysis had pure phase. The $\text{LiGd}_{0.05}\text{Mn}_{1.95}\text{O}_4$ precursor completely crystallized at 600°C . The particle nature of the prepared thin films was uniformly distributed. The average particle size of $\text{LiGd}_{0.05}\text{Mn}_{1.95}\text{O}_4$ was around 89 nm. The charge/discharge curves at the 1st and 25th cycle of $\text{Li//LiGd}_y\text{Mn}_{2-y}\text{O}_4$ ($y=0.01, 0.03, 0.05$) showed that the $\text{Li//LiGd}_{0.01}\text{Mn}_{1.99}\text{O}_4$ gave first

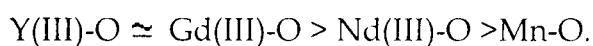
cycle discharge capacity of 137mAh/g, which faded to 124mAh/g in the 25th cycle, registering the capacity retention of 90.5%. The corresponding values for Li//LiGd_{0.03}Mn_{1.97}O₄ were 134mAh/g, 123mAh/g and 91.8% and for Li//LiGd_{0.05}Mn_{1.95}O₄ 126mAh/g, 115mAh/g and 91.2%, respectively. The initial discharge capacity fell down with an increase in the substituent content due to decrease in Mn³⁺ concentration with increase in y value of LiGd_yMn_{2-y}O₄. The capacity loss observed for Li//LiGd_yMn_{2-y}O₄ from y=0.01, 0.03, 0.05 are 9.5%, 8.2% and 8.8% respectively. Among the various compositions, LiGd_{0.03}Mn_{1.99}O₄ showed good electrochemical performance than the other compositions.

The prepared LiNd_yMn_{2-y}O₄ (y = 0.01, 0.03 and 0.05) thin film cathode materials by polymer spray pyrolysis had single phase with no impurities. The LiNd_{0.05}Mn_{1.95}O₄ precursor completely crystallized at 600°C. The particle nature of the prepared thin films was uniformly distributed. The average particle size of LiNd_{0.05}Mn_{1.95}O₄ was around 90 nm. The charge/discharge curves at the 1st and 25th cycle of Li//LiNd_yMn_{2-y}O₄ (y=0.01, 0.03, 0.05) showed that the Li//LiNd_{0.01}Mn_{1.99}O₄ gave first cycle discharge capacity of 136mAh/g, which faded to 123mAh/g in the 25th cycle, registering the capacity retention of 90.4%. The corresponding values for Li//LiNd_{0.03}Mn_{1.97}O₄ were 133mAh/g, 121mAh/g and 90.9% and for Li//LiNd_{0.05}Mn_{1.95}O₄ 126mAh/g, 113mAh/g and 89.6%, respectively. The initial discharge capacity fell down with an increase in the substituent content due to decrease in Mn³⁺ concentration with increase in y value of LiNd_yMn_{2-y}O₄. The capacity loss observed for Li//LiNd_yMn_{2-y}O₄ from y=0.01, 0.03, 0.05 are 9.6%, 9.1%

and 10.4%, respectively. Among the various compositions, $\text{LiNd}_{0.03}\text{Mn}_{1.99}\text{O}_4$ showed good electrochemical performance than the other compositions.

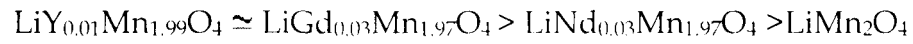
It can be concluded that the polymer spray pyrolysis could yield cubic spinel cathode material of lower particle size with enhanced electrochemical performance. Hence, polymer spray pyrolysis was the effective method for the preparation of cubic spinel thin film than the conventional method.

The substituted spinels such as $\text{LiY}_y\text{Mn}_{2-y}\text{O}_4$, $\text{LiGd}_y\text{Mn}_{2-y}\text{O}_4$ and $\text{LiNd}_y\text{Mn}_{2-y}\text{O}_4$ showed better electrochemical performance than the parent LiMn_2O_4 . Therefore, the prepared substituted spinel structure became more tolerant to the repeated charge-discharge cycles due to the doping of metal cation. This may be attributed to the reduction of Mn valency giving rise to the suppression of Jahn-teller distortion. Among the various dopant with various compositions, yttrium substituted lithium manganese oxide ($\text{LiY}_{0.01}\text{Mn}_{1.99}\text{O}_4$) and gadolinium substituted lithium manganese oxide ($\text{LiGd}_{0.03}\text{Mn}_{1.97}\text{O}_4$) showed good electrochemical performance with the capacity retention of 92% and 91.8%, respectively, compared to the capacity retention of $\text{LiNd}_{0.03}\text{Mn}_{1.97}\text{O}_4$ (90.9%). The better cycleability doped variety was due to the increased stability caused by higher octahedral site stabilisation energy of doped metal oxygen bond. So the bond enthalpy of Y(III)-O and Gd(III)-O is larger than the bond enthalpy of Nd(III)-O as shown in the following order:



Larger the bond enthalpy of metal-oxygen led to more stable crystal structure causing enhanced electrochemical performance.

Hence, the order of effective thin film cathode materials for Li-ion batteries is as follows:



It concludes that the yttrium substituted LiMn_2O_4 ($\text{LiY}_{0.01}\text{Mn}_{1.99}\text{O}_4$) and gadolinium substituted LiMn_2O_4 ($\text{LiGd}_{0.03}\text{Mn}_{1.97}\text{O}_4$) can be used as the promising positive thin film electrode materials for Li-ion microbatteries.